$[Sn(SO_3F)_6]$, 37477-90-0; $Sn(SO_3F)_4$, 28646-46-0; ClO_2SO_3F, 24114-30-5; $S_2O_6F_2$, 13709-32-5; $K_2[SnCl_6]$, 16923-42-5; $Cs_2[SnCl_6]$, 17362-93-5; $(NO)_2[SnCl_6]$, 30406-43-0.

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Heteropoly 12-Metallophosphates Containing Tungsten and Vanadium. Preparation, Voltammetry, and Properties of Mono-, Di-, Tetra- and Hexavanado Complexes[1,2]

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Alkali salts of the anions $PVW_{11}O_{40}{}^{4-}$ (I), $PV_2W_{10}O_{40}{}^{5-}$ (II), $HPV_4W_8O_{40}{}^{6-}$ (III), and $H_3PV_6W_6O_{40}{}^{6-}$ (IV) have been prepared and analyzed. Stationary-electrode voltammetry using wax-impregnated carbon and pyrolytic graphite electrodes has been used to characterize these complexes in solution. The anions I-IV undergo one-, two-, four-, and six-electron reductions, respectively, at potentials between +0.58 and −0.04 V *vs.* sce. The voltammograms are sufficiently characteristic to allow identification of these complexes in mixtures and to trace their reactions. The kinetics of conversion of I into II at pH 3.9 and 4.9 have been followed. The reaction is second order in I and is consistent with a hydrolytic disproportionation, a process which parallels reactions of heteropoly blues. Preparation of vanadium-containing heteropoly anions by the "etherate" method has been shown to give variable results.

Introduction

The existence of heteropoly anions containing simultaneously atoms of tungsten(VI), molybdenum(VI), and/or vanadium(V) has long been considered plausible. In particular, many examples of heteropoly complexes in which the atomic ratio of central atom P(As, Si, Ge):W(Mo) + V = 1:12 have been reported.[5-13] Following the determination of the structure of $PW_{12}O_{40}{}^{3-}$ in 1933,[14] it has tacitly been assumed that the materials described in ref 5-13 contained anions with the same ("Keggin") structure. While this is doubtless the case, the authenticity and chemical individuality of some of the reported "mixed heteropoly anions" remains dubious. In only a few cases have well-analyzed recrystallizable materials been described, and many conclusions about the existence of certain complexes have been based upon solution measurements, which are open to other interpretations. In the P-W-V and P-Mo-V systems, careful work by independent groups[11-13] has identified the complexes $PV_xW_{12-x}O_{40}{}^{n-}$ (x = 1, 2, 6, 10) and $PV_xMo_{12-x}O_{40}{}^{n-}$ (x = 1, 2, 3, 6, 10). Some earlier work[10] on the other hand only indicated the existence of complexes with x = 2.

The present work, originally undertaken in connection with our studies of heteropoly blues,[15] has resulted in the isolation and confirmation of the complex, $PV_4W_8O_{40}{}^{7-}$. This complex was specifically excluded in the scheme of P-V-W heteropoly anions proposed by Courtin,[13] although others have described materials that may have contained such an anion.[16,17] This paper also reports the first successful voltammetric studies of vanadium-containing polyanions; other investigators have used the dropping mercury electrode (dme) with consequent chemical reduction of vanadium(V) by mercury.

Experimental Section

Preparation of Complexes. The preparation of alkali salts of $Co^{II}W_{12}O_{40}{}^{6-}$, $SiW_{12}O_{40}{}^{4-}$, $PW_{12}O_{40}{}^{3-}$, and $P_2W_{18}O_{62}{}^{6-}$ has been described before.[18,19]

Ammonium (Potassium) 8-Tungsto-4-vanadophosphate. A solu-

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(3) Holder of an NSF Summer Award to Secondary School Teachers, 1965-1966; NIH Predoctoral Fellow, 1966-1968.

(4) Author to whom correspondence should be addressed.

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tion of 48.8 g of sodium metavanadate (0.40 mol) in 250 ml of water was added to a solution of 220.0 g of sodium tungstate (0.67 mol) in 250 ml of hot water, followed by 50 ml of concentrated phosphoric acid (0.67 mol). The resulting deep red solution was covered and heated to 95° for 1 hr. To the cold solution was added sufficient solid ammonium (potassium) chloride to initiate precipitation, and then further quantities of the cations were added in the form of saturated solutions of the chlorides. The products were recrystallized two or three times from 0.25 *M* sulfuric acid at 80°. *Anal.* Calcd for $(NH_4)_6HPV_4W_8O_{40}\cdot 9H_2O$: NH_3, 3.91; P, 1.18; V, 7.80; W, 56.22; H_2O, 8.63. Found: NH_3, 3.77; P, 1.17; V, 7.76; W, 56.3; H_2O (difference), 8.76; acidic H per P, 1.2. Atomic ratio NH_3:P:V:W = 5.9:1:4.0:8.1. Calcd for $K_5H_2PV_4W_8O_{40}\cdot 11H_2O$: K, 7.13; P, 1.13; V, 7.44; W, 53.65; H_2O, 7.92. Found: K, 7.01; P, 1.14; V, 7.56; W, 53.8; H_2O (weight loss at 170°) 7.22; H_2O (weight loss at 450°) 7.88; acidic H per P, 1.95. Atomic ratio K:P:V:W: = 4.1:1:4.0:8.0.

Ammonium 6-Tungsto-6-vanadophosphate. The procedure described for the preparation of ammonium 8-tungsto-4-vanadophosphate was followed using 55.0 g of sodium tungstate (0.17 mol) in 60 ml of water, 36.6 g of sodium metavanadate (0.30 mol) in 190 ml of water, and 25 ml of phosphoric acid (0.33 mol). The red-brown precipitate that formed on addition of ammonium chloride was not entirely soluble in hot 0.25 *M* sulfuric acid, but the solution yielded black truncated octahedra on cooling. These crystals were recrystallized twice from the 0.25 *M* sulfuric acid before being ground and allowed to effloresce to an equilibrium hydrate. *Anal.* Calcd for $(NH_4)_5H_4PV_6W_6O_{40}\cdot 6H_2O$: NH_3, 3.73; P, 1.36; V, 13.41; W, 48.34; H_2O, 8.33. Found: NH_3, 3.76; P, 1.33; V, 12.93; W, 48.95; H_2O (difference), 8.44; acidic H per P, 1.8. Atomic ratio NH_3: P:V:W = 5.2:1:5.9:6.2.

10-Tungsto-2-vanadophosphates. Samples of the acid $H_5PV_2W_{10}O_{40}$ were prepared following the procedure of Kokorin,[20] which involves an ether extraction. The method did not give strictly reproducible materials, as indicated by analytical V:W ratios. A typical analysis follows. *Anal.* Calcd for $H_5PV_2W_{10}O_{40}\cdot 12H_2O$: P, 1.09; V, 3.60; W, 64.90; H_2O, 9.31. Found: P, 1.22; V, 3.79; W, 64.14; H_2O (weight loss at 170°), 7.26; H_2O (weight loss at 450°), 9.29; acidic H per P, 5.3. Atomic ratio P:V:W = 1:1.9:8.9. Addition of KCl to a solution of the acid gave at least two products (orange-red and yellow-orange needles). The orange-red product, upon recrystallization from 0.25 *M* sulfuric acid, proved to be the potassium salt, $K_5PV_2W_{10}O_{40}$. *Anal.* Calcd for $K_{4.7}H_{0.3}PV_2W_{10}O_{40}\cdot 9H_2O$: K, 6.22; P, 1.05; V, 3.45; W, 62.2; H_2O, 5.48. Found: K, 6.21; P, 1.00; V, 3.43; W, 62.12; H_2O (weight loss at 170°), 4.61; H_2O (wt loss at 450°), 5.01; acidic H per P, 0.4. Atomic ratio P:V:W = 1:2.1:10.4.

Potassium 11-Tungsto-1-vanadophosphate. A pure sample of this salt was obtained, undoubtedly fortuitously, during the course of a sequence of ether extractions described below. *Anal.* Calcd for $K_4PVW_{11}O_{40}\cdot 5H_2O$: K, 5.23; P, 1.04; V, 1.70; W, 67.74; H_2O, 3.00. Found: K, 5.24; P, 1.04; V, 1.72; W, 67.75; H_2O, 3.07. Atomic ratio K:P:V:W = 4.0:1:1.0:11.0. Attempts to prepare this compound directly from 11-tungstophosphate[21] and metavanadate ions always produced materials low in vanadium. Solutions containing $PVW_{11}O_{40}{}^{4-}$ as the predominant species could be prepared by equilibrating mixtures of $HPV_4W_8O_{40}{}^{6-}$ and $PW_{12}O_{40}{}^{3-}$; see below.

Analytical Procedures. The potentiometric and spectrophotometric methods used for vanadium and tungsten have been described elsewhere.[22] Phosphorus was determined gravimetrically following a triple precipitation as magnesium ammonium phosphate. Potassium and barium were weighed as the tetraphenylborate and sulfate, respectively. Ammonia was determined by a Kjeldahl distillation. Acidic protons were determined by potentiometric titration at 0° with CO_2-free sodium hydroxide. Equilibrium potentials were established rapidly and the end points were sharp. Little interference from slow depolymerization reactions was experienced at this temperature.

Electrochemical Measurements. (a) Apparatus. Since vanadium-containing polyanions are reduced at potentials positive to the oxidation potential of mercury, solid microelectrodes were used in the voltammetric studies. The electrodes used were as follows.

(1) Rotating Platinum (Rpe), Sargent No. S-30420, Rotated at 600 Rpm by Means of a Synchronous Motor. Pretreatment consisted of cathodic evolution of hydrogen in 0.1 *M* sulfuric acid for 10 sec followed by rinsing in distilled water.

(2) Pyrolytic Graphite (Pyge). A 12-cm cylinder, 9 mm in diameter, of pyrolytic graphite (Type EPC-G-1 from General Electric, Metallurgical Products Department, Detroit, Mich.) was mounted in a Pyrex tube with epoxy cement. Pretreatment consisted of rinsing with distilled water. The use of a wetting agent recommended by Elving, *et al.*,[23] was found not to be necessary to ensure reproducible behavior.

(3) Wax-Impregnated Graphite (Wige), Prepared as described by Elving and Smith,[24] and Mounted in a Glass Tube. Pretreatment followed that used for the pyge, with the exception that rinsing with 0.003% Triton X-100 preceded the final water rinse.

A two-electrode system with Sargent Model XV and FS instruments and in later work a three-electrode system with Heath operational amplifier based modules were used. Measurements were made at 25.0 ± 0.1° except where otherwise stated. All quoted potentials refer to the saturated calomel electrode.

(b) Stationary Electrode Voltammetry of Heteropolytungstates. As a preliminary test the behavior of several heteropoly anions, known from dme or rpe polarographic studies to undergo one- and two-electron changes, was examined using the pyge and the Sargent XV instrument at a voltage sweep rate of 3.33 mV sec^{-1}.

The one-electron oxidation of $Co^{II}W_{12}O_{40}{}^{6-}$ to $Co^{III}W_{12}O_{40}{}^{5-}$ was observed at a peak potential of +0.92 V in a 0.01 m*M* solution, 1.0 *M* sodium sulfate, pH 3.7. The cathodic peak was observed at +0.86 V, in satisfactory agreement with the theoretical separation of 59 mV for a reversible oxidation. The corresponding potentials for 1.0 m*M* solutions were +0.94 V (anodic) and +0.86 V (cathodic). One-electron reductions[12,13] of $P_2W_{18}O_{62}{}^{6-}$ (both isomers), $SiW_{12}O_{40}{}^{4-}$, and $PW_{12}O_{40}{}^{3-}$ appeared increasingly irreversible, in that order, insofar as the separation of anodic and cathodic peaks was concerned. The peak separations were 60 mV for 0.10 m*M* $P_2W_{18}O_{62}{}^{6-}$, 120 mV for 0.2 m*M* $SiW_{12}O_{40}{}^{4-}$, 190 mV for 2.0 m*M* $SiW_{12}O_{40}{}^{4-}$ (all in 1.0 *M* sodium sulfate, pH 2.3), and 220 mV for 1.0 m*M* $PW_{12}O_{40}{}^{3-}$ in 1.0 *M* H_2SO_4. A more detailed investigation of the 12-tungstophosphate reduction is reported elsewhere.[25]

The second and third reduction steps of $P_2W_{18}O_{62}{}^{6-}$ in acidic solutions are both two-electron processes according to dme and rpe polarography and potentiometry.[19] On the pyge these "two-electron" processes gave peak potentials that were double the height of a one-electron reduction, with a separation of the cathodic and anodic peaks of 60–70 mV. These results indicate a superposition of two reversible one-electron steps rather than a single two-electron reduction since the latter would have given a peak height of $2^{3/2}$ times that for a one-electron reduction.[26]

Spectroscopy. Uv and visible spectra were recorded in quartz cells on a Cary Model 14 instrument.

Results and Discussion

Properties of the 8-Tungsto-4-vanadophosphate Anion. The chemical individuality of this complex, prepared in the form of ammonium and potassium salts as described in the Experimental Section, was established in the following ways. (1) Samples of the potassium salt were recrystallized twice from 0.25 and 0.05 *M* sulfuric acid and were analyzed following each recrystallization. The results of recrystallization from 0.05 *M* acid were unsatisfactory—after two recrystallizations the analytical V:W ratio had fallen from 1.99 to 1.90. On the other hand, recrystallization from 0.25 *M* acid had no effect upon V:W, although a more acid salt was produced. After recrystallization from 0.25 *M* acid the ratio H:4V had increased from 0.50 to 1.36 and there was a corresponding decrease in the K content. (2) Solutions containing the free acid $H_7PV_4W_8O_{40}$ were prepared by ion exchange on Dowex 50 resin at 0°. Under these conditions the recovery of vanadium was 98.5%. The uv spectrum of the effluent from the ion-exchange column was identical with that of the original salt. Titration of the acid solution at 0° with sodium hydroxide showed two end points, the first (at pH 4–5) after 6 equiv and the second (pH 7–10) after

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[20] A. I. Kokorin, *Zh. Obshch. Khim.*, 24, 967 (1954).

[21] See, for example, C. Tourne and G. Tourne, *Bull. Soc. Chim. Fr.*, 1124 (1969).

[22] D. P. Smith and M. T. Pope, *Anal. Chem.*, 40, 1906 (1968).

[23] L. Chuang, I. Fried, and P. J. Elving, *Anal. Chem.*, 36, 2427 (1964); W. R. Turner and P. J. Elving, *ibid.*, 37, 467 (1965).

[24] P. J. Elving and D. L. Smith, *Anal. Chem.*, 32, 1849 (1960).

[25] D. P. Smith and M. T. Pope, in preparation.

[26] R. Adams, "Electrochemistry at Solid Electrodes," Marcel Dekker, New York, N. Y., 1969.

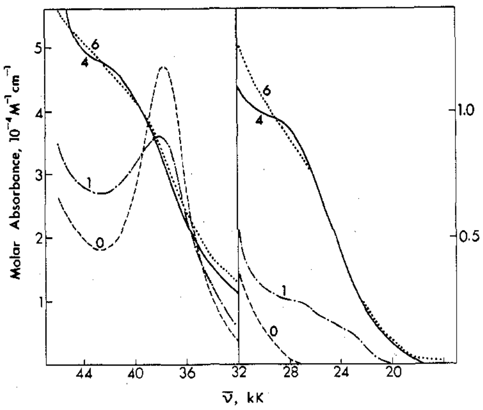

Figure 1. Electronic spectra of 0.02 m*M* solutions of $PVW_{11}O_{40}{}^{4-}$ (1), $HPV_4W_8O_{40}{}^{6-}$ (4), and $H_3PV_6W_6O_{40}{}^{6-}$ (6) in 1.0 *M* sodium sulfate, pH 2.2. The spectrum of $PW_{12}O_{40}{}^{3-}$ (0) in 1.0 *M* sulfuric acid is included for comparison.

the seventh equivalent of base had been added. Since the pH readings were established rapidly through the second end point, we conclude that the second end point *does* indicate a deprotonation rather than a hydrolysis reaction. Results consistent with the acid titrations were found in titrations of all acid salt samples prepared. For example, $K_5H_2PV_4W_8O_{40}$ gave end points at 0.87 and 1.95 equiv of base per mole of heteropoly anion. (3) The electronic spectrum (Figure 1) of solutions of the potassium and ammonium salts in various buffer solutions was insensitive to moderate changes of pH within the range 0 (1 *M* H_2SO_4) to 7.[27] Within this range the spectrum had shoulders at *ca.* 235 and 335 nm. In more acidic solutions (3 *M* H_2SO_4) and at pH 9.3 (NH_3 buffer) the spectrum decayed with time indicating partial or complete decomposition. At pH 2-7 small (0-4%) changes were noted in the absorbances after some hours. In 0.02 *M* H_2SO_4-0.98 *M* Na_2SO_4 Beer's law was obeyed within 2% at 340 nm over the concentration range 5.0-0.050 m*M*. At 235 nm deviations of 10-20% were noted however. Molar absorptivities, measured in 0.02 m*M* solutions, were 4.8 × 10^4 and 9.8 × 10^3 M^{-1} cm^{-1} at 235 and 335 nm, respectively.

Properties of the 6-Tungsto-6-vanadophosphate Anion. This anion was prepared only in the form of an ammonium salt,[28] although a solution of the free acid was successfully prepared by ion exchange at 0°. Recovery of vanadium in the ion-exchange experiment was 98.5%. Titration of the acid solution at 0° yielded end points after 6 and 7 equiv of base had been added. A third neutralization step was indicated but after a further 0.6 equiv of base had been added (*i.e.*, 7.6 equiv in all), drifting of the pH readings started, indicating the onset of hydrolytic degradation (pH 9.8).[29]

The electronic spectrum of 0.02 m*M* solutions of the ammonium salt was similar in appearance and intensity (see Figure 1) to that of the 8-tungsto-4-vanadophosphate anion, although the shoulders were less pronounced.

Spectrum of the 11-Tungsto-1-vanadophosphate Anion. The spectrum of solutions of $K_4PVW_{11}O_{40}$ in 1.0 *M* sodium sulfate, pH 2.2, shows shoulders at 355 and 410 nm and a maximum at 262 nm. Beer's law was strictly obeyed at 355 and 410 nm, and within 10% at 262 nm, over the concentration range 4.0-0.025 m*M*. The molar absorptivities were 1.5 × 10^3 and 2.6 × 10^3 M^{-1} cm^{-1} at 410 and 355 nm, respectively. In 4.0 m*M* solution, the molar absorptivity at 262 nm was 3.75 × 10^4 M^{-1} cm^{-1}

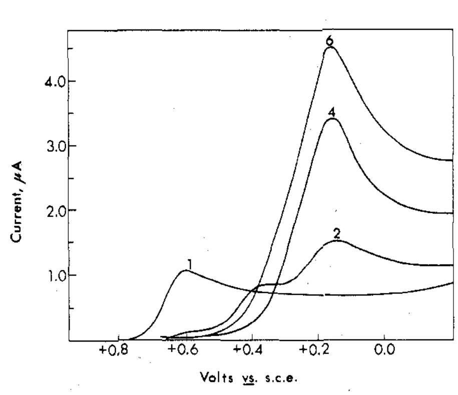

Figure 2. Cathodic sweep voltammograms (pyge) of $PVW_{11}O_{40}{}^{4-}$ (1), $PV_2W_{10}O_{40}{}^{5-}$ (2), $HPV_4W_8O_{40}{}^{6-}$ (4), and $H_3PV_6W_6O_{40}{}^{6-}$ (6). Depolarizer concentration 0.10 m*M* in 1.0 *M* sulfate, pH 2.3.

Table I. Effect of Voltage Scan Rate upon Peak Potential and Current of $PVW_{11}O_{40}{}^{4-}$ in 0.8 *M* $NaClO_4$ + 0.2 *M* Acetate Buffer, pH 2.3

Concn of depolarizer, m*M*	0.2 V min^{-1}		0.5 V min^{-1}	
	E_p, V	i_p, μA	E_p, V	i_p, μA
1.0	0.61	3.20	0.60	5.04
0.4	0.60	1.52	0.59	2.24
0.2	0.59	0.76	0.58	1.24
0.1	0.58	0.40	0.57	0.70

Voltammetric Characterization of Tungstovanadophosphates. Electrochemical data for the mixed heteropoly anions are summarized in Tables I-IV and illustrated in Figure 2. These data are condensed from much more extensive measurements.[30] For 8-tungsto-4-vanadophosphate and 6-tungsto-6-vanadophosphate anions on the carbon electrodes reproducible electrochemical behavior could be ensured only if fresh portions of solutions were used for duplicate runs and if, above pH 3, the solutions were freshly prepared. Repeated voltage sweeps of the same solutions led to gradual decay of the voltammograms and occasionally to the appearance of new reduction steps.

Discussion of the behavior of individual anions follows.

(a) 11-Tungsto-1-vanadophosphate. This anion undergoes a one-electron reduction at *ca.* + 0.6 V corresponding to the reaction $PV^VW_{11}O_{40}{}^{4-} + e^- \rightarrow PV^{IV}W_{11}O_{40}{}^{5-}$.[31] No further reduction processes occur until *ca.* −0.6 V where tungsten atoms are reduced.[31] The vanadium reduction is essentially reversible, *e.g.*, using the wige at 25° with 0.10 m*M* heteropoly anion in 1 *M* sulfate, pH 2.3, at 0.5 V min^{-1}, E_p = +0.57 V, separation of cathodic and anodic peaks 80mV, and reciprocal slope[32] of the reduction peak 64 mV. However, both peak potential and peak current are affected by concentration and voltage scan rate; see Table I.

The effect of pH upon E_p, other factors being constant, is rather small, indicating that protonation does not accompany the reduction process. It is difficult to assess the pH effect quantitatively for (as discussed below) at pH 3 and above the voltammogram decays with time, and in more acidic solu-

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[27] According to the voltammetric studies, the pH range of stability is shorter.

[28] P. Courtin and P. Souchay, *C. R. Acad. Sci., Ser. C*, 270, 1714 (1970), described the preparation of the potassium salt.

[29] This value does not signify that the anion is stable up to pH 9.8 at 0°. The purpose of the pH titrations was to determine numbers of acidic protons. The titrations depend for their success upon rapid deprotonations and do not yield equilibrium data.

[30] D. P. Smith, Ph.D. Dissertation, Georgetown University, 1972.

[31] D. P. Smith, H. So, J. Bender, and M. T. Pope, *Inorg. Chem.*, in press. See also Abstracts, 158th National Meeting of the American Chemical Society, New York, N. Y., 1969, No. INOR 190.

[32] Reciprocal slope $V/[\log((i_p - i)^{1/2}/i)]$.

Table II. Voltammetric Data for $PV_2W_{10}O_{40}^{5-}$, 0.10 m*M* in 1.0 *M* Sulfate at 25° (Pyge, Voltage Scan Rate 0.2 V min^{-1})

pH	E_p, V	ΔE,[a] mV	i_{pc},[b] μA	i_{pa}/i_{pc}[c]
(1 *M* H_2SO_4)	+0.34	120	2.1	0.80
1.23	~+0.37		1.6	
	~+0.23			
2.25	+0.37	60	0.7	0.56
	+0.18	130	0.8	1.20
3.73	+0.37	80	0.8	0.80
	+0.07	130	0.8	1.00
4.85	+0.37	80	0.8	0.80
	~0	180	0.6	0.95

[a] Separation of cathodic and anodic peaks. For a reversible *n*-electron reduction, $\Delta E = 59/n$ mV. [b] Cathodic peak current. Since this depends upon electrode surface area, it is included only for comparison with values in Tables III and IV. [c] Ratio of anodic to cathodic peak currents. For a reversible reduction $i_{pa}/i_{pc} = 1.00$.

tions there is evidence of establishment of equilibrium among $PVW_{11}O_{40}^{4-}$, $PV_2W_{10}O_{40}^{5-}$, and $PW_{12}O_{40}^{3-}$. At pH 1 (1 *M* sulfate) and in 1 *M* sulfuric acid, the peak has shifted to +0.52 V. A slight negative shift in acidic solutions of an otherwise pH-independent reduction has also been observed in dme polarograms of $PW_{12}O_{40}^{3-}$, $SiW_{12}O_{40}^{4-}$, and $P_2W_{18}O_{62}^{6-}$.[18,19] We attribute this to a diminution of the extent of adsorption of the reduced species in the more acidic solutions. Similar effects (diminished anodic wave heights for reduced anions) have been observed with $SiW_{12}O_{40}^{4-}$ for example,[18,33] and Herve has noted that the anodic waves of $SiW^V{}_3W_9O_{40}^{7-}$ were restored to the correct height and their half-wave potentials shifted to more negative potentials in the presence of tetramethylammonium ion.[34] The explanation must correspond to that given here, namely, that the large organic cation is specifically adsorbed on the electrode, and adsorption of the heteropoly anion is blocked.

(b) 10-Tungsto-2-vanadophosphate. As mentioned in the Experimental Section, analyses of samples containing $PV_2W_{10}O_{40}^{5-}$ were never wholly satisfactory. However, voltammograms of all samples were sufficiently consistent in their general features to permit characterization of the anion. As shown in Table II, the anion undergoes a two-electron reduction in 1 *M* sulfuric acid, but as the pH of the solution is raised, the single peak splits into two one-electron steps. This behavior corresponds to that of many heteropoly anions[18,19,35] and signifies that protonation of the reduced species occurs in acid solutions. Thus, in 1 *M* H_2SO_4

$$PV_2W_{10}O_{40}^{5-} + 2e^- + H^+ \rightarrow HPV^V{}_2W_{10}O_{40}^{6-} \text{ (or } H_2PV_2W_{10}O_{40}^{5-}\text{)}$$

and at pH ≥2-3

$$PV_2W_{10}O_{40}^{5-} + e^- \rightarrow PV^{IV}VW_{10}O_{40}^{6-} \quad (E_p = +0.37\ \text{V})$$

$$PV^{IV}VW_{10}O_{40}^{6-} + e^- \rightarrow PV^{IV}{}_2W_{10}O_{40}^{7-} \quad (E_p = 0.0\ \text{V})$$

The anion is extensively decomposed in solution above pH 5. Voltammograms of the different samples of $PV_2W_{10}O_{40}^{5-}$ at, for example, pH 2.3, all showed the two reductions at +0.37 and +0.18 V, but the relative heights of the peaks varied somewhat from sample to sample. In addition, most samples showed traces of a reduction at +0.57 V indicating contamination with $PVW_{11}O_{40}^{4-}$.

(c) 8-Tungsto-4-vanadophosphate and 6-Tungsto-6-vanadophosphate. In their pH range of stability (0 to *ca.* 7) both of these anions showed single irreversible reductions, the peak currents being respectively 4 and 6 times that expected for a one-electron process, when measured under the same conditions of pH and supporting electrolyte; see Tables III and IV.[36] Since, in stationary-electrode voltammetry, the peak height of an *n*-electron reduction is proportional[26] to $n^{3/2}$, the data in Tables III and IV suggest that the reductions involve a sequence of one-electron steps at virtually identical potentials. Both E_p and $E_{1/2}$ for these heteropoly anions shifted to more negative values as the pH increased. This behavior indicates that protonation accompanies reduction, as for other tungstates of high initial charge.[18]

Table III. Voltammetric Data for 0.10 m*M* Solutions of $HPV_4W_8O_{40}^{6-}$ in 1 *M* Sulfate at 25° (Pyge, Voltage Scan Rate 0.2 V min^{-1})

pH	E_p, V	ΔE, mV	i_{pc}, μA	i_{pa}/i_{pc}
(1 *M* H_2SO_4)	+0.34	120	4.2	0.55
1.23	+0.23	125	3.4	0.80
2.25	+0.18	125	3.4	0.90
3.73	+0.08	120	3.4	0.95
4.85	−0.02	130	2.3	1.00

Table IV. Voltammetric Data for 0.10 m*M* Solutions of $H_3PV_6W_6O_{40}^{6-}$ in 1 *M* Sulfate at 25° (Pyge, Voltage Scan Rate 0.2 V min^{-1})

pH	E_p, V	ΔE, mV	i_{pc}, μA	i_{pa}/i_{pc}
(1 *M* H_2SO_4)	+0.34	130	5.6	0.48
1.23	+0.26	145	4.7	0.59
2.25	+0.18	135	4.5	0.64
3.73	+0.06	170	4.1	0.80
4.85	−0.04	190	3.2	0.88

The reductions of $HPV_4W_8O_{40}^{6-}$ and $H_3PV_6W_6O_{40}^{6-}$ are irreversible, as seen from the data in Tables III and IV and from the variation of *E* and i_p with voltage sweep rate and concentration. For example, at pH 2.3 (1.0 *M* Na_2SO_4) E_p = +0.18 V (0.10 m*M*) and 0.14 V (0.10 m*M*).

Variation of E_p with Charge. In spite of the irreversibility of many of the reductions, we note that the peak potentials depend upon anionic charge in a linear fashion. For 0.10 m*M* solutions, 0.2 V min^{-1} sweep rate, 1.0 *M* sodium sulfate supporting electrolyte, and pH 2.3, the peak potentials are as follows (V): $PVW_{11}O_{40}^{4-}$, +0.57; $PV_2W_{10}O_{40}^{5-}$, +0.37; $HPV_4W_8O_{40}^{6-}$, $H_3PV_6W_6O_{40}^{6-}$, +0.18. A similar variation of reduction potential with charge for heteropoly 12-tungstates has been observed,[18] and an electrostatic model was discussed.

Reactions of the 11-Tungsto-1-vanadophosphate Anion. Voltammograms of $PVW_{11}O_{40}^{4-}$ in acid solutions (pH <1) show, upon standing, traces of new reductions at *ca.* +0.4 and 0.0 V; see Figure 3. The figure also shows the shift toward negative potentials of the reduction of $PVW_{11}O_{40}^{4-}$ at +0.5-0.6 V. The reason for this shift was discussed above. The reduction at 0.0 V almost certainly indicates the presence of $PW_{12}O_{40}^{3-}$ in these acid solutions, and the peak at *ca.* +0.4 V may be due to $PV_2W_{10}O_{40}^{5-}$. A partial conversion of $PVW_{11}O_{40}^{4-}$ to $PW_{12}O_{40}^{3-}$ in acid solutions would parallel reactions observed by Baker, *et al.*,[37] and subsequent workers for the 1:1:11 tungsto species containing di- and trivalent metal atoms, *e.g.*

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(33) P. Souchay and G. Herve, *C. R. Acad. Sci.*, 261, 2486 (1965).

(34) G. Herve, *C. R. Acad. Sci., Ser. C*, 263, 413 (1966).

(35) R. Massart and G. Herve, *Rev. Chim. Miner.*, 5, 501 (1968).

(36) Rpe polarograms of $HPV_4W_8O_{40}^{6-}$ were consistent with the data of Table III, the half-wave potential of the irreversible four-electron wave being +0.240 ± 0.005 V in 1.0 *M* sulfate, pH 2.3, for example.

(37) L. C. W. Baker, V. E. S. Baker, K. Eriks, M. T. Pope, M. Shibata, O. W. Rollins, J. H. Fang, and L. L. Koh, *J. Amer. Chem. Soc.*, 88, 2329 (1966); L. C. W. Baker and J. S. Figgis, *ibid*, 92, 3794 (1970).

$$12[(H_2O)CoO_5SiO_4W_{11}O_{30}]^{8-}\ (\equiv SiW_{11}CoO_{40}H_2{}^{8-}) \xrightarrow{H^+} 11SiW_{12}O_{40}{}^{4-} + 12Co^{2+} + SiO_2$$

Further evidence indicating that $PV_2W_{10}O_{40}{}^{5-}$ is more stable than $PVW_{11}O_{40}{}^{4-}$ under acidic conditions is presented below in the discussion of the etherate method of isolating heteropoly anions.

Above pH 3 the voltammogram of $PVW_{11}O_{40}{}^{4-}$ is gradually transformed into that of $PV_2W_{10}O_{40}{}^{5-}$; see Figure 4. The rate of disappearance of $PVW_{11}O_{40}{}^{4-}$, determined from the height of the peak at +0.57 V, in well-buffered solutions follows second-order kinetics for several half-lives. A typical plot is shown in Figure 5. The rates are both pH and ionic strength dependent. Half-lives of $PVW_{11}O_{40}{}^{4-}$ at 25° were 4.0 hr (pH 3.9, 1.0 *M* sulfate), 7.4 min (pH 4.9, 1.0 *M* sulfate), and 39 min (pH 4.9, 0.2 *M* sulfate) and correspond to rate constants of 0.69, 22.4, and 4.3 M^{-1} sec^{-1}, respectively. These figures provide the first kinetic data supporting the "hydrolytic disproportionations" proposed for several heteropoly and isopoly anions.[13,19,35] In the present case it may be presumed that the equilibrium

$$2PVW_{11}O_{40}{}^{4-} \leftrightarrow PV_2W_{10}O_{40}{}^{5-} + PW_{12}O_{40}{}^{3-}$$

is displaced to the right through the very rapid[38] conversion of $PW_{12}O_{40}{}^{3-}$ into $PW_{11}O_{39}{}^{7-}$ above pH 1.5. However, the strong pH dependence of the rate shows that the mechanism involves hydrolysis in the early stages of the reaction. A more complete study is in progress. It is noteworthy that the disproportionation of the tungstovanadates is analogous to those observed for heteropoly blues, *e.g.*

$$2PW^VW_{11}O_{40}{}^{4-} \rightarrow PW^V{}_2W_{10}O_{40}{}^{5-} + (PW_{12}O_{40}{}^{3-}), \text{ etc.}^{19}$$

Reactions of 8-Tungsto-4-vanadophosphate. Voltammograms of mixtures of $HPV_4W_8O_{40}{}^{6-}$ and $PW_{12}O_{40}{}^{3-}$ which had been allowed to equilibrate (2 weeks at room temperature or 6 hr at 95°) show that extensive formation of other tungstovanadophosphates occurred in these solutions, even under conditions where $PW_{12}O_{40}{}^{3-}$ is normally considered to be hydrolytically stable. With a 1:3 mole ratio of $HPV_4W_8O_{40}{}^{6-}$ to $PW_{12}O_{40}{}^{3-}$ in 1 *M* sulfuric acid for example, the final solution contained approximately 85 mol % $PVW_{11}O_{40}{}^{4-}$ (measured by its reduction at +0.52 V) and traces of $PV_2W_{10}O_{40}{}^{5-}$ and $PW_{12}O_{40}{}^{3-}$ (peaks at +0.37 and 0.0 V, respectively); see Figure 6. Similar results were obtained at pH 2.3, but there was no apparent reaction between $HPV_4W_8O_{40}{}^{4-}$ and $SiW_{12}O_{40}{}^{4-}$, $BW_{12}O_{40}{}^{5-}$, or $H_2W_{12}O_{40}{}^{6-}$ under these conditions.

If equimolar mixtures of $HPV_4W_8O_{40}{}^{6-}$ and $PW_{12}O_{40}{}^{3-}$ were taken in an attempt to synthesize $PV_2W_{10}O_{40}{}^{5-}$, the equilibrated solutions at pH 2.3 contained large fractions of $PVW_{11}O_{40}{}^{4-}$ (40-60 mol %) and of $PV_2W_{10}O_{40}{}^{5-}$ (20-50 mol %), together with quantities of a species reduced between +0.18 and 0.0 V. The last species may be unreacted $HPV_4W_8O_{40}{}^{6-}$ or the trisubstituted anion $PV_3W_9O_{40}{}^{6-}$ which would be expected to be reduced at a similar potential in view of its charge.

With a 3:1 starting ratio, *i.e.*, stoichiometrically correct for $PV_3W_9O_{40}{}^{6-}$, the equilibrated solutions in 1.0 *M* sulfate at pH 2.3 showed a small reduction at +0.37 V ($PV_2W_{10}O_{40}{}^{5-}$) and a much larger peak at +0.13 V which could indicate the presence of $PV_3W_9O_{40}{}^{6-}$ and/or unchanged $HPV_4W_8O_{40}{}^{6-}$. No evidence for $PVW_{11}O_{40}{}^{4-}$ was found in the solutions equilibrated at pH 2.3, although this species was present in solutions equilibrated in 1.0 *M* sulfuric acid.

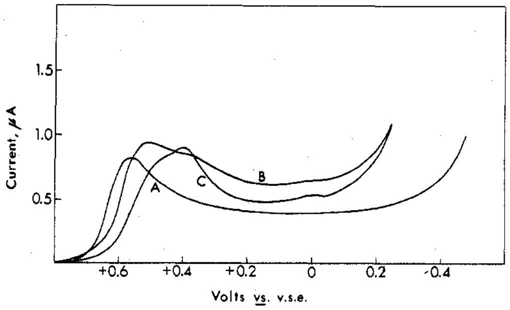

Figure 3. Cathodic sweep voltammograms (wige) of 0.10 m*M* solutions of $PVW_{11}O_{40}{}^{4-}$ aged 24 hr at room temperature. Supporting electrolyte: A, 1.0 *M* sulfate, pH 2.3; B, 1.0 *M* sulfuric acid; C, 3.0 *M* sulfuric acid.

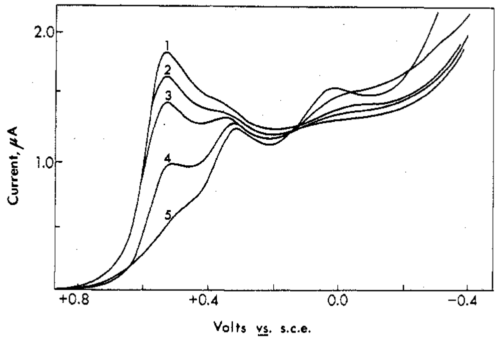

Figure 4. Effect of time on the voltammogram of 0.10 m*M* $PVW_{11}O_{40}{}^{4-}$ in 1.0 *M* sulfate, pH 3.9. Ages of solutions 1-5: 25, 75, 125, 305, and 1085 min.

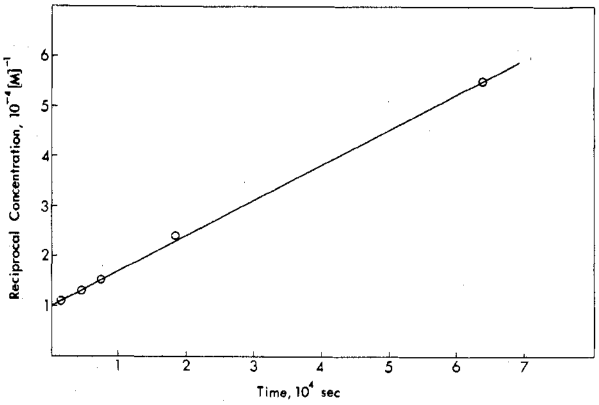

Figure 5. Second-order rate plot for the disappearance of $PVW_{11}O_{40}{}^{4-}$ in 1.0 *M* sulfate, pH 3.9, at 25°.

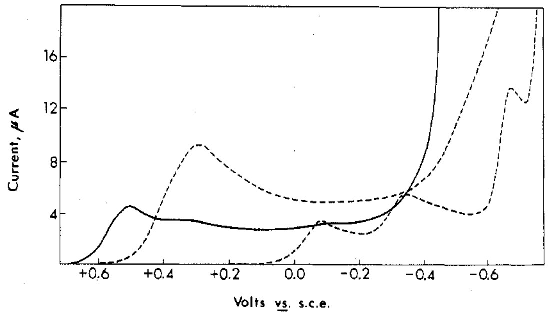

Figure 6. Voltammogram of a solution (at 25°) of $HPV_4W_8O_{40}{}^{6-}$ (0.25 m*M*) and $PW_{12}O_{40}{}^{3-}$ (0.75 m*M*) in 1.0 *M* sulfuric acid after storage for 6 hr at 95°. Broken lines show voltammograms of unreacted constituents, diminished in height by a factor of 2 for convenience.

The "Etherate" Method for Isolation of Heteropoly Tungstovanadophosphates. The formation of a liquid "etherate"

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[38] G. Schwarzenbach, G. Geier, and J. Littler, *Helv. Chim. Acta*, 45, 2601 (1962).

by ether extraction from strongly acidic solutions has become a fairly standard procedure for the isolation of heteropoly anions with the Keggin structure.[39] In the case of anions containing vanadium this method is unreliable as the following results show. It was noted in the reported preparations of $PV_2W_{10}O_{40}{}^{5-}$, which involve the etherate procedure, that solutions containing a threefold excess of vanadium and a large excess of phosphorus were used. In our hands, the colors of these solutions prior to ether extraction depended upon the amount of acid added. Etherates varying from yellow to deep red were obtained as the solutions became more acidic.

In one experiment, a solution of Na_2WO_4, $NaVO_3$, and H_3PO_4 in the mole ratio 10:2:10 was prepared, heated to 95° for 1 hr or so, allowed to cool, and treated with successive portions of 6 *M* sulfuric acid. Etherates were prepared from this solution at total acidities of *ca.* 2.0, 2.5, 3.0, 3.5 *M*, etc. The colors of the etherates were respectively yellow, deep yellow, orange, orange-red, and thereafter red. The etherates were decomposed by addition of water, the ether was removed in an air current, and potassium salts were isolated by addition of potassium chloride to the solutions of the heteropoly acids thus formed. The yellow product from the first etherate proved, upon analysis, to be a pure sample of $K_4PVW_{11}O_{40}$ (see Experimental Section). The other products were not quantitatively analyzed, but single-sweep voltammograms (wige) of solutions of several of these materials are illustrated in Figure 7. These voltammograms clearly show the appearance of two peaks at *ca.* +0.37 and 0.13 V (probably due to $PV_2W_{10}O_{40}{}^{5-}$) at the expense of the peak at +0.58 V ($PVW_{11}O_{40}{}^{4-}$) in the products obtained under more acidic conditions. These results demonstrate the fractionation of heteropoly anions that can occur during the etherate process of isolation, and they provide a possible explanation for the inability of Kokorin, *et al.*,[10] to observe complexes with only one vanadium atom.

Conclusions

The present work confirms the existence of several vanadium-containing heteropoly tungstates and demonstrates the value of stationary-electrode voltammetry for identifying some of these complexes in solutions and tracing their reactions. In general, the complexes are particularly sensitive to both acid- and base-induced hydrolysis, a property which in some cases prevents the isolation of homogeneous, stoichiometric materials. In the particular system studied here $PV_xW_{12-x}O_{40}{}^{(3+x)-}$, complexes where $x = 1, 2, 4$, and 6 have been characterized. Other workers[13,40] have also reported complexes where $x = 10$ and 12[41] and there would seem to be no reason to doubt the existence of the other members of the series. However, anions with even numbers of vanadium atoms seem to be more stable than those with odd numbers, as shown by the reactions of $PVW_{11}O_{40}{}^{4-}$ reported above. Why this should be so is not clear to us at present, but we note an analogy with the heteropoly blues. Under acid conditions heteropoly tungstates and molybdates undergo only two- or four-electron reductions to give anions with even numbers of W(V) or Mo(V) atoms.

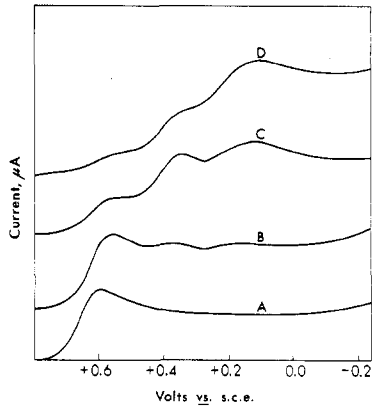

Figure 7. Cathodic sweep voltammograms of materials obtained from etherates described in the text. Equal weights of potassium salts (13.8 mg) precipitated from acids obtained by ether extraction were dissolved in 50 ml of 1.0 *M* sodium sulfate, pH 2.2. Approximate acidities prior to etherate formation and colors of the products: A, 2 *M*, yellow; B, 3 *M*, dark yellow; C, 4 *M*, orange; D, 5 *M*, red.

Registry No. $(NH_4)_6HPV_4W_8O_{40}\cdot 9H_2O$, 12-773-205; $K_5H_2PV_4W_8O_{40}\cdot 11H_2O$, 12-773-216; $(NH_4)_5H_4PV_6W_6O_{40}\cdot 6H_2O$, 12-773-227; $H_5PV_2W_{10}O_{40}\cdot 12H_2O$, 12-773-181; $K_5PV_2W_{10}O_{40}$, 12-773-192; $K_4PVW_{11}O_{40}\cdot 5H_2O$, 12-773-170; $Co^{II}W_{12}O_{40}{}^{6-}$, 12-181-054.

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(39) See, for example, P. Souchay, "Ions Mineraux Condenses," Masson et Cie., Paris, 1969, pp 90–93.

(40 A. Rosenheim and M. Pieck, *Z. Anorg. Chem.*, **98**, 223 (1916); P. Souchay and S. Dupois, *Ann. Chim. (Paris)*, **3**, 88 (1948); R. Ripan, A. Duca, and V. Cordis, *Rev. Roum. Chim.*, **12**, 375 (1967).

(41) For complexes where $x > 6$, the observed basicity is always less than $3 + x$. It is therefore possible that the anions contain fewer than 40 oxygen atoms, *e.g.*, $PV_{12}O_{36}{}^{7-}$, although it is difficult to devise a satisfactory structure for such a condensed species.